

Gas phase structures of alkali-cationized cereulide responsible for regioselective dissociation by collisional activation, effect of the missed ions

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Emetic toxin is increasingly reported worldwide for its involvement in *Bacillus cereus* food poisoning outbreaks. The preformed toxin in food called cereulide is a heat-stable cyclodepsipeptide, [(^D)Ala-O(^L)Val-(^L)Val-O(^D)Leu]₃ and an ionophore selective to K⁺ in solution. In electrospray (ESI), the K⁺ selectivity is reduced since the Li⁺, Na⁺, NH₄⁺ adduct ions are also detected in competition without adding salt to introduced sample solutions.

Here, by infusing synthetic cereulide into ESI positive ion source, Li⁺/Na⁺/K⁺ cationized cereulide coexists in two forms: charge-solvated (CS) form and protonated salt (PS). Various high resolution tandem instruments based on resonant (LTQ/Orbitrap) and non-resonant (Qq/TOF, Qq/Orbitrap) excitations were used. Energy resolved mass spectrometry breakdowns (ERMS, 0 eV to 150 eV) were compared for different involved alkali cation ions to highlight coexisting forms.

The [M+Li]⁺, [M+Na]⁺ and [M+K]⁺ ions within PS form dissociate through covalent bond cleavages resulting in alkali retention in the **a**, **b** ion series accompanied by exotic product ions, detected with tandem based on TOF and Orbitrap analyzers. From [M+K]⁺, a lot of product ions are lost from the latter analyzer compared to those detected using the former. Indeed, the lost ions are essentially K⁺ (for Orbitrap, m/z scale is ≥ m/z 50). This behavior differs to that observed for [M+Li]⁺ and [M+Na]⁺, which does not display Li⁺ and abundant Na⁺ using Qq/TOFMS. The direct K⁺ loss occurs only from the cationized cereulide within CS form. This is confirmed by the sequential MS³ experiments on the [M+K]⁺, [M+Li]⁺, and [M+Na]⁺ product ions that display exclusive 2nd generation product ions with K⁺/Li⁺/Na⁺ retention. This suggests that the CS form is favored for [M+K]⁺ and conversely for [M+Li]⁺ and [M+Na]⁺. The existence of the missed alkali cation (vide supra) is highlighted by the loss of the total ionic current compared to that observed during the dissociation of [M+NH₄]⁺. Finally, consideration of the various currents (total ion, product ion, alkali cation) based on the absolute abundances [1] will be discussed as well as the different product ion series.

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References

Hueber A. et al. J. Am. Soc. Mass Spectrom. 2023, 34, 1, 36–4.